



Article Iron Isotope Composition of Adakitic Rocks: The Shangcheng Pluton, Western Dabie Orogen, Central China

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Abstract: There has been little research on the metal isotopic composition of adakitic rock. The main objective of our investigation was to obtain more knowledge on the iron isotopic composition of adakitic rocks and provide new evidence for the genesis of Shangcheng pluton from an iron isotope perspective. The Dabie orogen is divided into eastern and western areas by the Shangcheng-Macheng fault, and the Shangcheng pluton is located in the western Dabie orogen area. The iron isotopic composition of these rocks ranges from 0.08% to 0.20% (2SD, n = 3). The δ^{56} Fe values of two rocks from the SGD (Sigudun) unit are relatively low ($0.11 \pm 0.03\%$ and $0.08 \pm 0.04\%$), while the δ^{56} Fe values of the other samples are basically consistent (0.18–0.2‰). Evidence from elemental geochemical characteristics and petrogenesis defines the Shangcheng pluton as adakitic rocks. Our investigation on the elemental and isotopic compositions hints that the enrichment of heavy iron isotopes cannot be explained by weathering/alteration and fluid exsolution. Fractional crystallization of magnetite may account for the enrichment of light iron isotopes in two rocks from the SGD unit, while the fractional iron isotope trend in the other five samples can be explained by Δ^{56} Fe_{crystal-melt} = ~0.035‰. Two investigated rocks from SGD units may have been derived from the partial melting of amphibolite, while the other five samples may have been derived from the partial melting of eclogite containing 10-15% garnet.

Keywords: Dabie orogen; adakitic rocks; iron isotopes; source rock mineralogy

1. Introduction

Recent theoretical developments have revealed that the fractionation of iron isotopes occurs during magmatic processes. Partial melting, fractional crystallization, and fluid exsolution can all be responsible for the enrichment of heavy iron isotopes [1–13]. Nevertheless, factors besides magmatic processes can also cause significant fractionation of iron isotopes. Due to the different mineral compositions of the source rock, the δ^{56} Fe value of melt generated by the molten lower crust in the eastern Dabie orogen ranges from 0.120‰ to 0.196‰, according to simulations and observations, contributing to the heterogeneity of δ^{56} Fe after crystallization [14]. Redox conditions also account for the fractionation of iron isotopes. Li et al. [15] reported that the δ^{56} Fe content of the Archaean BIF deposit is 1.5–2.6‰, due to a low degree of Fe (II) oxidation along with very low oxidation rates, resulting in the enrichment of heavy iron isotopes. On the contrary, Fe³⁺ released from primary minerals will form secondary minerals under an oxidative environment, preventing a loss of Fe and a change in the iron isotopic composition [16,17].

A popular explanation of adakites is that they originated from partial melting of subducted slab, which endows them with a unique geochemical composition compared with general granitic rocks ($Al_2O_3 \ge 15\%$, Sr > 300 ppm, Y < 20 ppm, unobvious Eu anomaly, etc.) [18]. It should be noted that there are genetic differences between adakite and adakitic



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). rocks. The genesis of adakitic rocks generally involves four methods: (1) partial melting of the lower crust; (2) partial melting of the delaminated crust; (3) differentiation of mafic magma under high pressure; and (4) mixed magma [19]. The above four types of adakitic rocks have been confirmed or reported [20–25].

Previous studies on adakitic rocks have been mainly based on the geochemical characteristics of major and trace elements. However, few studies have been conducted on its metal isotopes. In this study, the iron isotopic composition and elemental content of seven adakitic rocks from the Shangcheng pluton were measured. Considering the complexity of iron isotopic fractionation, the effects of weathering/alteration and fluid exsolution on isotopic fractionation are first discussed by assessing the elemental and iron isotopic features. Then, the contributions to isotopic enrichment of fractional crystallization and the mineral composition of the source rock are evaluated by modelling, and evidence on the elemental and isotopic connection is revealed. The main objective of our investigation is to obtain more knowledge on the iron isotopic composition of adakitic rocks and gain new evidence on the genesis of the Shangcheng pluton from an iron isotope perspective.

2. Geological Setting

The Dabie orogen is located at the Central China Orogenic, which is in the eastern part of the Qinling-Tongbai orogen (see Figure 1) [26]. It formed when the South China block subducted beneath the North China block during the Triassic and resulted in volcanic activity during the Cretaceous [27–35]. A large volume of intrusive intermediate-acid magma provides us a good chance to research the iron isotope composition of adakitic rocks. The Shangcheng-Macheng fault divides the Dabie orogen into eastern and western areas (Figure 1), and the Shangcheng pluton is located in the western area of the Dabie orogen.



Figure 1. Geological map of the western Dabie orogen (modified after [36,37]).

The Shangcheng pluton contains the Guishan Formation, Nanwan flysch Unit, Yangxiaozhuang Formation, and Xiaojiamiao Formation, and it is covered by late Cretaceous Jingangtai volcanic rocks [27]. Previous studies have divided the Shangcheng pluton into Sigudun (128–137 Ma), Shiguwa (130–139 Ma), and Loufangwan (133–141 Ma) intrusive units, according to their textures, mineral compositions, and contact relationships [38–41] (Figure 2). We named these the SGD unit (Sigudun), SGW unit (Shiguwa), and LFW unit (Loufangwan).



Figure 2. Simplified geological map of the Shangcheng pluton (modified after [38]).

A porphyritic texture can be observed in SGD unit samples, and the phenocryst is dominated by potassium feldspar, which accounts for about 20% of the total content. The matrix is dominated by plagioclase (35%) and quartz (25%). Biotite (5–10%) and amphibole (5%) can be seen under single polarizer (3a), as can accessory minerals, such as apatite and magnetite (Figure 3a–c). A porphyritic-like structure can be observed in samples from the SGW unit, and potassium feldspar dominates the phenocrysts (20%). The matrix includes plagioclase (30%), quartz (30%), biotite (5%), and hornblende (Figure 3d–f). Some plagioclase has a ring structure (Figure 3e). Large potassic feldspar crystals (Figure 3h,i) can be seen locally in samples from the LFW unit. Quartz, plagioclase, and biotite are encapsulated in the potassic feldspar phenocrysts (Figure 3g,h). The matrix is dominated by quartz (30%) and plagioclase (30%), with small amounts of biotite (5%), apatite, and magnetite.



Figure 3. Representative field photographs and photomicrographs (single and crossed polars) of the

Shangcheng pluton. (**a**,**d**) are samples of the SGD unit and SGW unit viewed under a single polar microscope. They include apatite, hornblende, biotite, magnetite, and other mineral particles; (**b**,**e**,**h**) are specimen photographs of the SGD unit, SGW unit, and LFW unit, respectively. A xenolith with a diameter of about 1 cm can be seen in the SGW unit; (**c**) shows the main rock-forming minerals, which are potassium feldspar, plagioclase, and quartz under crossed polar; (**f**) is a sample from the SGW unit, showing the ring structure of plagioclase; (**g**) is from the LFW unit and shows rock-forming minerals, such as quartz and potassium feldspar; (**i**) is a microscopic photo of giant potassium feldspar; Pl—plagioclase; Qtz—quartz; Am—amphibole; Bt—biotite; Mag-magnetite; Ap—apatite.

3. Analytical Method

Twenty-three samples were collected from the Shangcheng pluton, and seven samples were selected for this study by excluding the altered samples (SGD unit: SGD-2-1, SGD-2-3, SGD-3-1; SGW unit: SGW-1-2; LFW unit: LFW-1-1, LFW-1-2, LFW-2-1).

Major element analyses of whole rock were conducted on XRF (Primus II, Rigaku, Japan) at the Wuhan Samplesolution Analytical Technology Co., Ltd., Wuhan, China, and the analysis error was less than 1% (except P_2O_5). Trace element analyses of whole rock were conducted with an Agilent 7700e ICP-MS at the Wuhan SampleSolution Analytical Technology Co., Ltd., Wuhan, China. For the specific process followed, see [42].

Iron isotope analyses of samples were conducted at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, China. Detailed descriptions of sample digestion, chemical evaporation, and other chemical procedures are given in [43]. Iron isotopic measurements were performed on a Nu Plasma 1700 MC-ICP-MS using the sample-standard bracketing (SSB) method. Dissolved IRMM-014 Fe isotope standard with 5 μ g g⁻¹ Fe was used as the bracketing standard, and the internal precision was better than 15 × 10⁻⁶ (relative standard error) for the ⁵⁶Fe/⁵⁴Fe ratio. Iron isotopic compositions were reported using the standard per mil (‰) notation of δ^{56} Fe for the ⁵⁶Fe/⁵⁴Fe ratio and δ^{57} Fe for the ⁵⁷Fe/⁵⁴Fe ratio, where:

$$\delta^{56} \text{Fe} = \left[({}^{56} \text{Fe} / {}^{54} \text{Fesample}) / ({}^{56} \text{Fe} / {}^{54} \text{Fe}_{\text{IRMM-014}}) - 1 \right] \times 1000 \tag{1}$$

$$\delta^{57}$$
Fe = [(⁵⁷Fe/⁵⁴Fesample)/(⁵⁷Fe/⁵⁴Fe_{IRMM-014}) - 1] × 1000 (2)

4. Results

4.1. Elemental Composition

The major and trace element compositions for these rocks are summarized in Tables 1 and 2. Samples from the Shangcheng pluton were generally found to be metaluminous, but one (LFW-1-2) was weakly peraluminous.

Table 1. Major element compositions of of Shangcheng adakitic rocks.

Composition (wt.%)	SGW-1-2	SGD-2-1	SGD-2-3	SGD-3-1	LFW-1-1	LFW-1-2	LFW-2-1	GBW07103
SiO ₂	67.64	68.43	69.65	67.29	70.87	71.30	71.89	73.01
TiO ₂	0.49	0.40	0.37	0.52	0.33	0.30	0.28	0.30
Al ₂ O ₃	15.54	15.38	15.25	15.23	14.76	14.96	14.45	13.45
TFe_2O_3	2.85	2.80	2.15	3.65	1.97	1.83	1.73	2.18
MnO	0.04	0.06	0.02	0.06	0.03	0.03	0.03	0.06
MgO	0.96	1.21	0.71	1.58	0.59	0.53	0.49	0.41
CaO	2.40	2.75	2.03	3.03	1.56	1.17	1.47	1.58
Na ₂ O	4.69	4.14	4.73	4.07	4.53	4.49	4.51	3.07
K ₂ O	3.78	4.16	4.04	3.94	4.27	4.70	4.15	4.97
P_2O_5	0.20	0.14	0.15	0.19	0.12	0.11	0.10	0.09
LOI	0.97	0.43	0.31	0.40	0.27	0.65	0.32	0.78
Mg#	40.21	46.33	39.74	46.33	37.30	36.85	36.34	
Fe ³⁺ /∑Fe	38.85	37.16	38.85	37.60	42.31	40.19	39.39	
(Na + K)/(Mg + Ca)	1.73	1.40	2.21	1.15	2.80	3.58	3.03	
A/CNK	0.96	0.94	0.96	0.92	0.99	1.02	0.99	
A/NK	1.31	1.36	1.25	1.39	1.22	1.20	1.21	

Composition (ppm)	SGW-1-2	SGD-2-1	SGD-2-3	SGD-3-1	LFW-1-1	LFW-1-2	LFW-2-1
Li	11.64	24.40	8.78	17.15	29.47	18.20	27.05
Be	1.68	2.05	1.95	1.92	3.09	2.58	2.86
Sc	4.12	5.19	3.08	7.12	2.58	2.77	2.87
V	43.71	46.87	32.10	59.63	24.49	23.29	20.83
Cr	5.57	16.84	3.43	19.42	5.26	4.25	3.58
Со	5.17	6.47	2.35	8.55	3.05	2.71	2.67
Ni	3.73	7.18	2.86	9.13	3.43	2.86	2.69
Cu	2.44	6.71	2.21	3.02	1.69	1.45	1.60
Zn	58.30	48.21	28.06	46.59	50.89	47.44	46.06
Ga	22.49	19.30	22.27	20.04	22.98	23.53	23.51
Rb	68.16	110.99	85.33	102.02	119.62	131.36	133.38
Sr	1000	873	1195	702	698	546	613
Y	8.93	11.73	7.59	14.05	6.99	7.11	6.37
Zr	209	123	171	165	172	170	155
Nb	8.28	9.27	7.25	10.35	8.87	9.59	8.46
Sn	1.01	0.89	0.92	0.90	0.97	1.07	0.93
Cs	0.52	2.27	0.80	1.46	4.51	2.68	2.28
Ва	1956	1815	2102	1454	1649	1661	1326
Hf	5.19	3.52	4.60	4.45	4.84	4.64	4.52
Ta	0.48	0.66	0.43	0.71	0.59	0.67	0.59
Tl	0.38	0.61	0.49	0.54	0.75	0.84	0.82
Pb	21.30	29.91	26.83	24.29	31.92	31.79	35.16
Th	8.80	11.24	8.45	11.56	11.74	10.87	12.13
U	1.54	2.88	1.91	2.22	2.00	2.24	3.40
La	57.82	32.22	44.82	40.57	49.07	40.44	37.74
Ce	98.37	61.43	80.33	75.01	85.89	74.12	67.33
Pr	10.37	6.67	8.58	8.29	9.06	7.86	6.98
Nd	37.08	24.57	29.69	30.93	31.27	27.51	24.90
Sm	5.54	3.82	4.54	4.84	4.48	4.19	3.74
Eu	1.56	1.16	1.17	1.33	1.19	1.04	0.94
Gd	3.59	2.93	2.87	3.63	2.87	2.69	2.22
Tb	0.40	0.40	0.33	0.47	0.31	0.29	0.25
Dy	2.00	2.14	1.53	2.70	1.48	1.34	1.23
Ho	0.31	0.38	0.24	0.47	0.23	0.21	0.20
Er	0.70	1.07	0.61	1.27	0.54	0.51	0.50
Tm	0.09	0.15	0.08	0.18	0.08	0.07	0.07
Yb	0.59	0.99	0.52	1.26	0.46	0.44	0.43
Lu	0.08	0.16	0.07	0.19	0.07	0.07	0.07
REE	218.52	138.09	175.37	171.14	187.01	160.80	146.61
LREE/HREE	27.14	15.82	27.10	15.83	29.90	27.53	28.44
Eu	1.00	1.02	0.93	0.93	0.95	0.89	0.92
(La/Yb)n	70.03	23.30	61.35	23.13	75.70	66.14	62.26
(Dy/Yb)n	2.26	1.44	1.95	1.44	2.13	2.05	1.9
CIA	48.97	48.49	49.02	48.02	49.72	50.60	49.76
Ba/Th	222.19	161.50	248.79	125.82	140.45	152.84	109.31
Nb/U	5.38	3.22	3.80	4.66	4.44	4.29	2.49
Rb/La	1.18	3.44	1.90	2.51	2.44	3.25	3.53
Zr/Hf	40.26	34.82	37.26	37.11	35.52	36.55	34.33
Th/U	5.73	3.90	4.43	5.20	5.88	4.86	3.57
Nb/Ta	17.11	14.06	16.91	14.54	14.96	14.42	14.42
Sr/Y	111.98	74.39	157.45	49.95	99.83	76.79	96.28
(Yb)n	3.48	5.84	3.08	7.40	2.73	2.58	2.56

 Table 2. Trace element compositions of Shangcheng adakitic rocks.

The samples from the Shangcheng pluton had high concentrations of SiO₂ (67.29~71.89%), Al₂O₃ (14.45~15.54%), and Na₂O (4.07~4.73%), along with low concentrations of Fe₂O₃^T

 $A_{12}O_3$ (14.45~15.54%), and Na_2O (4.07~4.75%), along with low concentrations of $Fe_2O_3^{-1}$ (1.73~3.65%) and $P_2O_5(0.10~0.20\%)$. The A/CNK (Al_2O_3 / ($CaO + Na_2O + K_2O$) mole ratio)

of the samples ranged from 0.92 to 1.02. The Mg# values ((Mg/Mg + Fe) mole ratio) ranged from 36.34 to 46.33.

The total REE content of the Shangcheng pluton ranged from 138.09 to 218.5 ppm, exhibiting LREE enrichment and unobvious Eu anomalies (δ Eu = 0.89–1.02) on chondritenormalized REE patterns (Figure 4a). On the primitive mantle-normalized trace element spider diagram (Figure 4b), it was observed that the samples were depleted of high-fieldstrength elements, such as P, Ti, Nb and Ta, while they were enriched in large ion lithophile elements, such as Pb, K, Ba.



Figure 4. Chondrite-normalized REE patterns (**a**) and primitive mantle-normalized trace element spider diagram (**b**). Chondrite and mantle-normalized values were taken from [44,45].

4.2. Iron Isotopic Composition

All seven samples had δ^{56} Fe concentrations ranging from 0.08‰ to 0.20‰ (2SD, n = 3) (Table 3). The δ^{56} Fe values of one sample (SGD-2-1 and SGD-3-1) were relatively low (0.11 \pm 0.03‰ and 0.08 \pm 0.04‰), while the δ^{56} Fe values of the other samples were in accordance (0.18–0.2‰). On the whole, the δ^{56} Fe content of the samples was in accordance with the trend of iron isotopic fractionation in granite.

Commlas	δ^{56} Fe vs.	IRMM014	δ^{57} Fe vs.		
Samples	Ave./‰	2SD/‰	Ave./‰	2SD/‰	11
SGW-1-2	0.18	0.01	0.25	0.04	3
SGD-2-1	0.11	0.03	0.18	0.06	3
SGD-2-3	0.17	0.02	0.22	0.04	3
SGD-3-1	0.08	0.04	0.12	0.09	3
LFW-1-1	0.18	0.04	0.27	0.07	4
LFW-1-2	0.19	0.02	0.30	0.03	3
LFW-2-1	0.20	0.04	0.29	0.07	2
BHVO-2	0.11	0.02	0.18	0.06	2
BCR-2	0.10	0.02	0.16	0.06	3

Table 3. Iron isotope compositions of representative samples.

5. Discussion

5.1. Petrogenesis of Shangcheng Pluton

After combining the mineralogy and elemental composition characteristics (Figure 5a,b), we propose that the Shangcheng pluton mainly includes two kinds of rocks: biotite monzonite and quartz monzonite.

A previous study [38] showed that the rock type of the Shangcheng pluton is high-K calc-alkaline I type granite, which originated from low-degree partial melting of eclogite or amphibolite in the presence of garnet. In this study, the Y-Sr/Y diagram (Figure 5c) shows that SGD-2-1 and SGD-3-1 may have a conjoint background. In the $(Yb)_n$ - $(La/Yb)_n$ diagram (Figure 5d), two points are also present at the junction. Those two anomalies will be discussed in a later chapter.



Figure 5. (a) A/CNK vs. ANK, (b) SiO_2 vs. $Na_2O + K_2O$ [46,47], (c) Y vs. Sr/Y [18], (d) (Yb)n vs. (La/Yb)_n [48]; the curves in Figure 5d indicate the degree of melting.

The Sr/Y-(La/Yb)_n (Figure 6a) and MgO-SiO₂ diagrams (Figure 6b) indicate that the investigated rocks used in this study may have originated from both thickened and delaminated lower crust through low-degree partial melting. All samples in this study are basically consistent with the compositional definition of adakite [18], with SiO₂ \geq 56 (wt.%), Al₂O₃ \geq 15 (wt.%), MgO \leq 3 (wt.%), Sr > 400 ppm, Sr/Y > 20, and no obvious Eu anomalies. Previous studies [38–41] have reached a consistent conclusion on the genesis of the Shangcheng pluton, which is that it was derived from the partial melting of mafic rocks in the lower crust. The Shangcheng pluton can be considered adakitic instead of adakite rocks, based on the genetic differences between them.



Figure 6. (a) Sr/Y vs. $(La/Yb)_n$ [21], (b) SiO₂ vs. MgO [49]. Curves 1, 2, and 3 in Figure 6a show batch partial melting with residual phases of 30% garnet + 69% clinopyroxene + 1% rutile (1), 15% garnet + 84.5% clinopyroxene + 0.5% rutile, (2), and 5% garnet + 94.9% clinopyroxene + 0.1% rutile (3). Segments on curves indicate 5% increments in the melt fraction.

5.2. Geological Information on the Iron Isotopic Composition

5.2.1. Weathering and Alteration

A slight alteration was presented in potassic feldspar, plagioclase, amphibole, and biotite, according to mineralogy observations (Figure 3c,e,f). This was found to be strongly connected to weathering and environmental alterations occurring after the magmatic process. Fe³⁺ is enriched in heavy iron isotopes due to its stronger bond strength, while Fe²⁺ is enriched in light iron isotopes as a result of its larger ionic radius and weaker bond strength [50–52]. Fe²⁺ is released from primary minerals under the influence of weathering and migrates with light iron isotopes. On the contrary, under strong oxidative conditions, the release of Fe³⁺ from primary minerals leads to the formation of secondary minerals, preventing the loss of Fe and fractionation of the iron isotope composition [17].

CIA (Chemical index of alteration, CIA = $Al_2O_3/(Al_2O_3 + Na_2O + K_2O + CaO)$, as a mole ratio, [53]) has been utilized to indicate the influence of the weathering degree on samples [54–56]. The δ^{56} Fe of the samples did not significantly change with increased weathering (Figure 7a,b). Ba and U, as fluid mobile elements, are found preferentially in fluid under weathering conditions, resulting in a decrease in Ba/Th and an increase in Nb/U. The evolving trend exhibited in the Ba/Th vs. δ^{56} Fe and Nb/U vs. δ^{56} Fe diagrams shows no connection between two indices (Figure 7c,d). The above results illustrate negligible effects of weathering and alteration on the δ^{56} Fe content of samples.



Figure 7. (a) CIA vs. δ^{56} Fe, (b) LOI vs. δ^{56} Fe, (c) Ba/Th vs. δ^{56} Fe, (d) Nb/U vs. δ^{56} Fe; data were taken from [17].

5.2.2. Fluid Exsolution

The solubility of water decreases with magmatic upwelling and a decrease in pressure, resulting in the exsolution of Fe²⁺-enriched fluids. The fluid carries away light iron isotopes and contributes to the enrichment of heavy iron isotopes in the residual magma [3,11,12]. The Zr/Hf of igneous rocks generally ranges from 26 to 46, but Zr is more likely to be enriched in F-bearing fluids than Hf [13], and same applies to Nb and Ta. Therefore, the exsolution of fluid causes Zr/Hf < 26 and Nb/Ta < 5 [13,57]. Both Rb and La and Th and U are incompatible pairs that are not significantly affected by magmatic processes. However, fluid exsolution will reduce the Rb/La value and increase the Th/U value due to the higher fluid mobility of Rb and U compared with that of La and Th [14,58].

A correlation was not observed between δ^{56} Fe and the four indices in this study (Figure 8a–d). On the Th/U vs. δ^{56} Fe diagram (Figure 8c), the Th/U of the samples

remains within the average Th/U value of the lower crust (~5.9 [14]) nearby. In addition, Du et al. [13] proposed that the control of iron isotope fractionation by fluid exudation is weak (<0.07‰). Therefore, fluid exsolution may not be the mechanism controlling the iron isotopic composition of the Shangcheng pluton.



Figure 8. (a) Rb/La vs. δ^{56} Fe, (b) Zr/Hf vs. δ^{56} Fe, (c) Th/U vs. δ^{56} Fe, (d) Nb/Ta vs. δ^{56} Fe. Data were taken from [12–14,56,58].

5.2.3. Fractional Crystallization and Mineralogy of the Source Rock

He et al. [14] reported the iron isotopic compositions of non-adakitic rock, low-Mg adakitic rock, and high-Mg Adak from the east Dabie orogen in Costa Rica/Panama, Central America and simulated the variation range of δ^{56} Fe melt-residual during the partial melting of low-Mg adakite. The (Dy/Yb)n vs. δ^{56} Fe diagram (Figure 9b) shows most samples plotted on the gray area, which may indicate the partial melting of eclogite containing 10~15% garnet, as the (Dy/Yb)n of melt = 1.9~2.3, δ^{56} Fe melt-residual = 0.067~0.089‰, and δ^{56} Fe melt = 0.138~0.155‰, according to previous simulation results [14]. This is similar to what can be observed on the (Yb)n vs. (La/Yb)_n diagram, which displays an origin from melted amphibolite containing 10% garnet (Figure 9a or Figure 5d). It is notable that SGD-2-1 and SGD-3-1 may stem from the partial melting of eclogite containing 5% garnet or amphibolite, as shown in the (Dy/Yb)n vs. δ^{56} Fe (Figure 9b) and (Yb)n vs. (La/Yb)n diagrams (Figure 9a or Figure 5d). The differences between the two samples from SGD and the other five samples suggest that the mineralogy of source rocks has had an effect on the fractionation of iron isotopes in the Shangcheng pluton.

In terms of the other five samples, the elemental results indicate that they may have been generated from the partial melting of amphibolite containing 10% garnet, while the iron isotope results suggest the partial melting from eclogite containing 10~15% garnet as the origin. We conclude that the latter origin is more likely. Firstly, previous studies have demonstrated that there were two periods of major magmatic processes in the Dabie orogen during the Mesozoic. Rock produced in the first period are aged 145–130 Ma and have the geochemical characteristics of adakitic rocks [33,59,60], while rock produced in the second period is aged 130~110 Ma and has the characteristics of ordinary granite [61–63]. The thinning of the lower crust is considered to have occurred 130 Ma ago [21,64]. According to the reported data [38–41], the age of SGD unit ranges from 128 Ma to 137 Ma, while the ages of the SGW unit (130–139 Ma) and the LFW unit (133–141 Ma) are both older than 130 Ma. Secondly, from the perspective of $(Dy/Yb)_n$, amphibole favours Dy over Yb. Thus, the $(Dy/Yb)_n$ should be lower if it was melted from amphibolite [21]. This may suggest that SGD-2-1 and SGD-3-1 were derived from the partial melting of amphibolite when the lower crust thinned with the removal of the eclogite source, while the other five samples may have been derived from the partial melting of eclogite containing 10~15% garnet, as the lower crust is still thickened with the existence of eclogite.



Figure 9. (a) $(Yb)_n$ vs. $(La/Yb)_n$ [48], (b) $(Dy/Yb)_n$ vs. δ^{56} Fe. The percentage denotes the content of garnet within the assumed source rock, and the blue dotted line is based on the simulative results from [14].

The δ^{56} Fe of the samples increased with an increasing Fe³⁺/ Σ Fe and decreasing Mg# (Figure 10a,b), suggesting that the crystallization fractionation may have an effect on the iron isotopic composition of the sample. In the SiO₂ vs. δ^{56} Fe diagram (Figure 10c), the crystallization trend is similar to what is displayed by reported data. δ^{56} Fe_{crystal-melt} can be simulated using the Rayleigh fractionation equation.

$$\delta^{56} \text{Fe}_{\text{melt}} = \delta^{56} \text{Fe}_{\text{melt}(0)} - \Delta^{56} \text{Fe}_{\text{crystal-melt}} \times \ln(f_{\text{Fe}})$$
(3)

where δ^{56} Fe_{melt(0)} represents the δ^{56} Fe value of the initial melt, and f_{Fe} represents the Fe fraction in the remaining melt (Figure 10d). Δ^{56} Fe_{crystal-mel} = ~0.035‰ may account for the fractional crystallization of most samples, apart from SGD-2-1 and SGD-3-1.



Figure 10. (a) Fe³⁺/ Σ Fe vs. δ^{56} Fe, (b) Mg# vs. δ^{56} Fe, (c) SiO₂ vs. δ^{56} Fe, (d) FeOt vs. δ^{56} Fe. The data were taken from [7,12,14,65]. The blue line stands for the modelled fractionation trend of samples.

Considering the $D_{Nb} / D_{Ta} = ~1$ in magnetite ($D_{Nb} = 2.2$, $D_{Ta} = ~2.5$; [66]), the fractional crystallization of magnetite may not lead to the variation of Nb/Ta (Figure 11a), but the concentration of Fe³⁺ or Fe₂O₃^T in the residual melt decreases as fractional crystallization proceeds, resulting in enrichment with heavy iron isotopes (Figure 11b). Thus, the fractional trend of iron isotopes in SGD-2-1 and SGD-3-1 may demonstrate the fractional crystallization of magnetite.



Figure 11. (a) Nb/Ta vs. δ^{56} Fe, (b) Fe₂O₃^T vs. δ^{56} Fe.

6. Conclusions

Evidence from the elemental geochemical characteristics and petrogenesis suggests that the Shangcheng pluton contains adakitic rock. Our investigation on the elemental and isotopic compositions hints that iron isotope enrichment cannot be explained by weathering/alteration and fluid exsolution. The fractional crystallization of magnetite accounts for enrichment with light iron isotopes in two rocks from the SGD unit due to the variation trends of Nb/Ta and Fe₂O₃^T, while the fractional trend of iron isotopes in the other five samples can be explained by Δ^{56} Fe_{crystal-melt} = ~0.035‰. Considering that one SGD unit sample was found to have evolved similarly to the SGW and LFW unit samples, it can be concluded that the other two SGD unit rocks are more likely to have been derived from the partial melting of amphibolite, while the other five samples may have been derived from the partial melting of eclogite containing 10–15% garnet.

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